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## Water Solubility of BIS (2-Ethylhexyl) Hydrogen Phosphite

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## WATER SOLUBILITY OF BIS (2-ETHYLHEXYL) HYDROGEN PHOSPHITE

### INTRODUCTION

Chemical warfare defense research routinely utilizes simulants for chemical agents. This substitutive approach offers several advantages. Specifically, procedures relying on simulants can be much less rigid and dangerous than those which use live agents. Simulants, in contrast to lethal agents, can be more readily disseminated in the open environment. Thus, with appropriate non-toxic simulants, one can contaminate a large piece of military equipment, and study the decontamination (simulant removal) of the impacted device in a non-lethal setting. Such a decontamination exercise would be profoundly more difficult if one were to use live chemical agents.

Chemical agent simulants are selected to match a variety of physical and chemical characteristics of live agents. In general, simulants are chosen to mimic one or more desired properties of the live agent. For example, researchers in the past have used such simulants as Malathion, benzene sulfonyl chloride or fluoride for G-agents, or chloroethyl-ethyl sulphide for mustard (HD). These simulants in part match the chemical reactivity of the agents. Other research has used simulants which closely match physical properties, (e.g., viscosity, density, or water solubility) of live agents. Specifically, methyl salicylate, a viscous fluid similar to VX, is a widely used simulant in part because it can be easily detected by its characteristic odor. Another frequently used VX simulant is BIS [BIS (2-ethylhexyl) hydrogen phosphite], which also exhibits physical properties similar to VX. VX has the following very unusual water solubilities: at 25°C, 3g VX per 100 g water; at 15°C, 7.5 g/100g; at 9.4°C, VX is infinitely miscible with water (J. Thompson, U. S. Army CRDEC, pers. comm. 1988). However, there are no data concerning the water solubility of BIS. This solubility information is important because the solubility of BIS will affect its ultimate utility as a simulant for VX. Manufacturers' and chemical suppliers' information indicate that BIS is "insoluble" in water. However, as very few substances are truly water-insoluble, it is appropriate to measure the water solubility of BIS, to confirm in part how well BIS matches the physical properties of VX. The results of this solubility investigation are reported here.

## EXPERIMENTAL

Saturated solutions of BIS in water were prepared by placing ~2 ml BIS, ( $[\text{CH}_3(\text{CH}_2)_3\text{CH}(\text{C}_2\text{H}_5)\text{CH}_2\text{O}]_2\text{P}(\text{O})\text{H}$ ,  $\text{C}_{16}\text{H}_{35}\text{O}_3\text{P}$ , f.w. = 306.4, Aldrich Chemical Co., Milwaukee, WI) into a 500 ml Pyrex breaker with ~300 ml of room-temperature (~23°C)  $\text{H}_2\text{O}$ . The BIS formed upper, distinct, thin, lens-like patches. The two phases were stirred vigorously with a magnetic stirrer for ~1 hour, with one hour phase separation before first sampling of the water for analysis. Later in the investigation, this room temperature system was stirred for some 15 minutes, with 1 hour phase separation, prior to each sampling.

Another aliquot of water was placed in a nest of ice/water in a larger container, and stirred to a low equilibrium temperature (~2°C) before adding the BIS. This system was stirred for one hour and the phases allowed to separate before taking water samples for analysis. A third aliquot of water was placed on a stirring hot plate to give an equilibrium temperature of ~92°C before addition of the BIS. This hot mixture was then stirred for one hour, with one hour for phase separation prior to sampling. Other aliquots were held at intermediate cold or hot temperatures to assess solubility at these temperatures. Cold and hot aliquots were discarded after subsampling for analysis; long term stability of BIS in contact with water was done at room temperature only.

The assay technique utilized in this study was to oxidize the dissolved organophosphorus compound BIS to phosphate ion. The resulting phosphate was quantified colorimetrically by monitoring the blue phosphomolybdate ion formed by reacting molybdate ion with the phosphate residual. The following reagent solutions were prepared for use in the dissolved BIS analyses.

Reagents (All solutions prepared in distilled water).

### 1. Potassium persulfate reagent:

Mix 15 ml of 9 N  $\text{H}_2\text{SO}_4$  (63 ml of conc.  $\text{H}_2\text{SO}_4$  + water to give 150 ml of room temperature solution) in 100 of ml water. Add 5 g of potassium persulfate ( $\text{K}_2\text{S}_2\text{O}_8$ ) and stir to dissolve. Store in a glass bottle and prepare fresh weekly.

### 2. Molybdate colorimetric reagent:

Mix 120 ml of 9N  $\text{H}_2\text{SO}_4$ , 45 ml of ammonium heptamolybdate solution (9.5 g of  $[\text{NH}_4]_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$  in 100 ml of water), 5 ml of potassium antimony tartrate solution (3.25 g of  $\text{K}[\text{SbO}]\text{C}_6\text{H}_4\text{O}_6$  in 100 ml of water) and 70 ml of water. This mixed solution is stored refrigerated (10°C) in a brown glass bottle, and is stable for several weeks.

### 3. Ascorbic acid reducing reagent:

Dissolve 7.0 g of ascorbic acid ( $C_6H_8O_6$ ) in 100 ml of water. Store at 10°C in a brown glass bottle until needed. This solution is stable for several weeks.

### 4. Phosphate standard stock solution:

Dissolve 0.136 g of  $KH_2PO_4$ , dried for 10 hours at 110°C in 100 ml of water ( $1.00 \times 10^{-4}$  M solution). 5.0 ml of this stock diluted to 500 ml gives a solution  $1.00 \times 10^{-6}$  M in phosphate, which can be diluted to give working standard solutions of  $1 \times 10^{-6}$  M to  $6 \times 10^{-6}$  M phosphate.

## ASSAY PROCEDURE

1.0 ml of saturated BIS solution (room temperature, cold, or hot) was pipetted into 35 ml of distilled water in each of several 125 ml Erlenmeyer flasks. 2.0 ml of persulfate oxidizing reagent were added, and the flasks closed with inverted 10 ml Erlenmeyer flasks. The samples were heated to incipient boiling on an electric hot plate for approximately 1/2 hour, then cooled to room temperature. 1.0 ml of molybdate colorimetric reagent was added to each sample with gentle swirling, then 1.0 ml of ascorbic acid reagent was added with gentle swirling. The molybdate blue color was allowed to develop for 10 to 15 minutes, and the absorbance of the solution measured at 880 nm. The absorbance of these DILUTED BIS solutions was compared with the absorbance of 35 ml phosphate standard(s) processed as above. Reagent blanks were 35 ml of distilled water, processed as above. Absorbance measurements were made with a 1 cm path length cell, for the BIS solutions, and 5 cm path length cells for the phosphate standards, with distilled water as the reference in both cases. This procedure is an adaptation of that reported by Grasshoff (1976).

## RESULTS

Data collected during this study are listed in Tables 1 and 2. The measured absorbance of the BIS solutions were compared with the absorbance of phosphate standards, which are plotted in Figure 1. The data show that a saturated BIS solution is  $\sim 700 \mu M$ , which converts to  $\sim 200$  ppm, for BIS in water at 23°C. At 2°C, BIS gives a  $300 \mu M$  (90 ppm) solution, while at 92°C, BIS dissolves to give a  $1300 \mu M$  (390 ppm) solution. See Figure 2 for a plot of solubility data.

The short-term stability data were collected over approximately three weeks, and show no evidence of hydrolysis of BIS (i.e., appearance in solution of increasing levels of soluble phosphorus hydrolysis products) in distilled water at 25°C and pH  $\sim 3$  (unbuffered) in that time period. This observed

stability of BIS should be considered whenever one contemplates using BIS for CBWD research, especially in light of the low, but measurable solubility of BIS in water, which is much less than reported for VX. However, after the BIS had been in contact with water for some 5 months, the BIS which collected on top of the water had turned light yellow. Furthermore, the aqueous phase as a solution which was approximately 2600  $\mu\text{M}$  in phosphate (Table 2), after persulfate oxidation of the dissolved organic matter. It would be useful to examine in detail the decomposition products of BIS in contact with water, and examine the interactions of BIS with the decontamination solutions used in CBW defense, tests beyond the scope of the present effort.

#### RECOMMENDATIONS

1. It would be useful to examine the solubility and stability of BIS in water solution as a function of buffered pH.

2. One should examine the reactivity of BIS with a variety of water soluble oxidizers such as hypochlorite ion, peroxide ion, and permanganate ion. This study would more completely define how well BIS mimics the chemical characteristics of CBW agents.

3. BIS reacts over a period of months with water. It would be useful to examine the reaction path and products of this interaction.

#### LITERATURE CITED

Grasshoff, Klaus (1976) Methods of Seawater Analysis. New York: Verlag Chemie, pp. 117-126.

TABLE 1

Solubility of BIS in Water as a Function of Temperature

<u>Temperature</u>	<u>Absorbance</u>	<u>Concentration, <math>\mu\text{M}</math></u>
$-2^{\circ}\text{C}$	0.14, 0.15, 0.14 0.21, 0.23 $\bar{x} = 0.17 \pm 0.04$	$300 \pm 70$
$-8^{\circ}\text{C}$	0.20, 0.19, 0.23 0.24, 0.22 $\bar{x} = 0.22 \pm 0.02$	$360 \pm 30$
$-23^{\circ}$	0.38, 0.34, 0.42 0.41 $\bar{x} = 0.39 \pm 0.03$	$700 \pm 50$
$-70^{\circ}\text{C}$	0.59, 0.54, 0.63 0.55, 0.61, 0.50 0.57 $\bar{x} = 0.57 \pm 0.04$	$1030 \pm 70$
$-92^{\circ}\text{C}$	0.72, 0.69, 0.76 0.70 $\bar{x} = 0.72 \pm 0.03$	$1300 \pm 50$



TABLE 2

Solubility of BIS as a Function of Time

<u>Sample</u> <u>Absorbance</u>	<u>Time in Solution (hr)</u>	
BIS in contact with water (~23°C)	Initial	0.38, 0.34, 0.41
		$\bar{x} = 0.39 \pm 0.04$
	200	0.45, 0.43
	360	0.46, 0.46
	550	0.46, 0.48
	5 months	1.43, 1.53, 1.56
		$\bar{x} = 1.51 \pm 0.07$
Blank (reagents)	-	0.03, 0.03

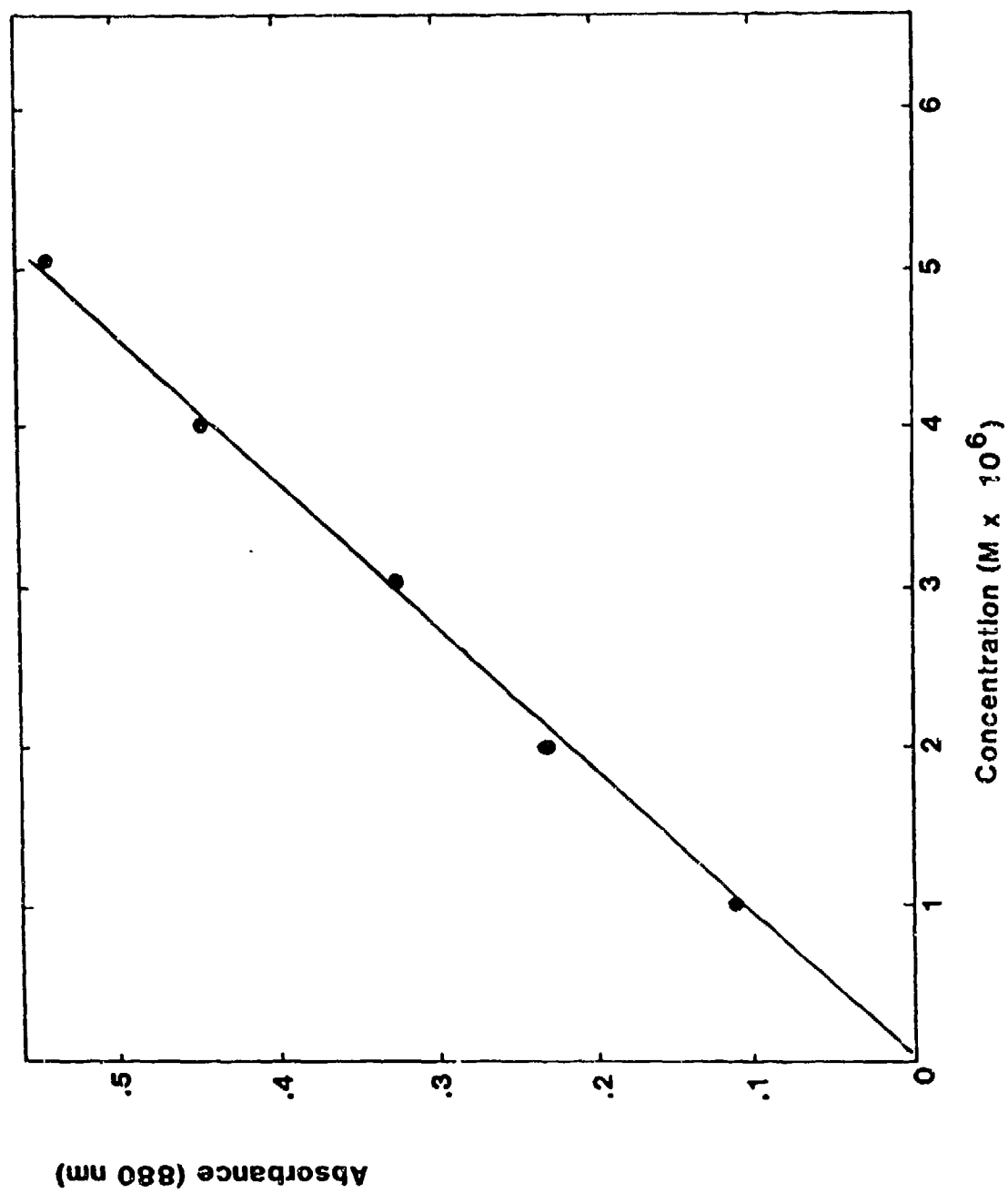


Figure 1. KH<sub>2</sub>PO<sub>4</sub> Colorimetric Calibration Curve

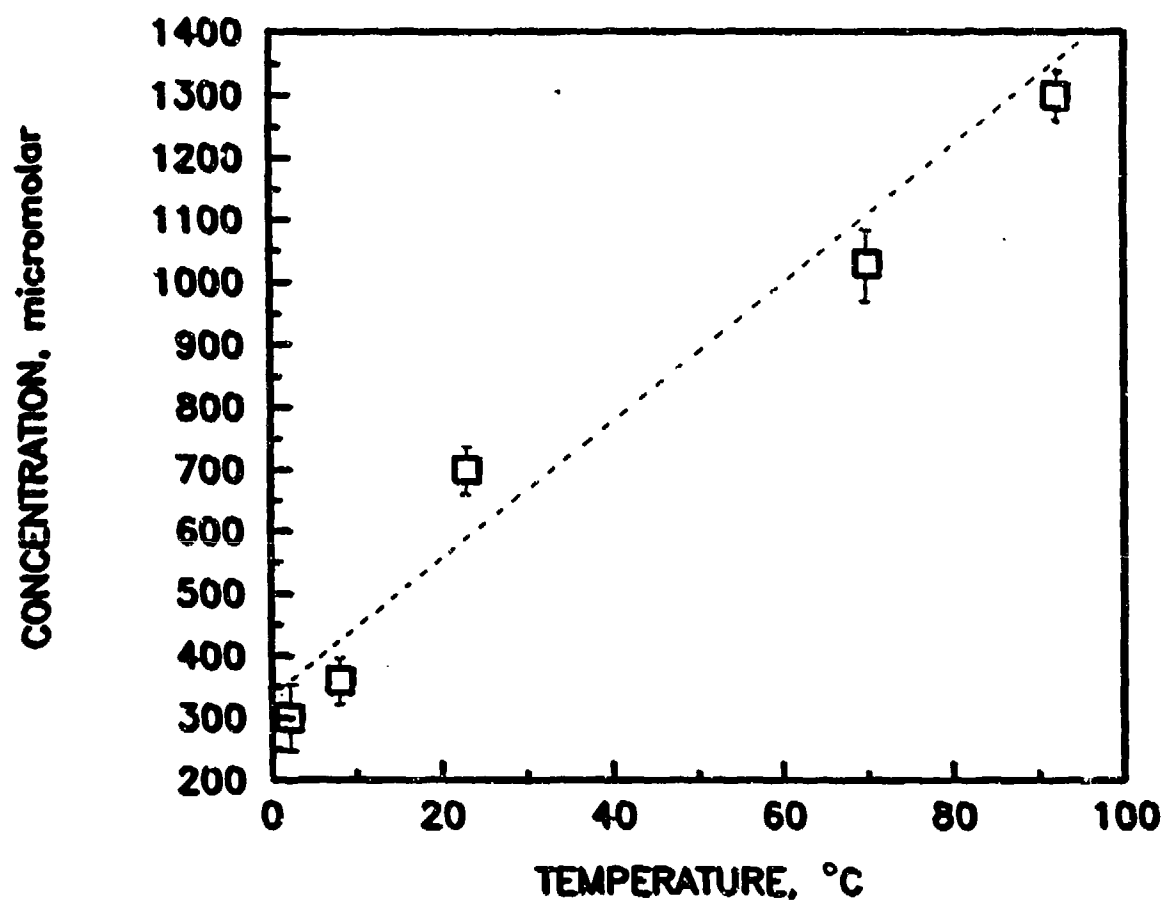


Figure 2. Solubility of BIS in Water